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We review briefly the singular perturbation problem arising in the approximate solution of diffusion from a large, neat, sessile agent droplet through a thin membrane. We obtain the zeroth order short time solution(which has a definite thickness scaling) but this solution is only valid for short times.

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Technical Report #12

# Diffusion through a membrane from a sessile droplet-limiting case

# of the large droplet approximation for short times.

by

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## 1. Introduction

Recently I have spent some effort on a grant supported by the U.S. Army Materials and Mechanics Research Center in studying numerically and analytically the diffusion of agent from a sessile agent droplet (a spherical cap) through the (polymer) membrane on which it rests. The agent droplet can be neat[1-4] or polymer thickened.[1,5,6] Dr. Nathaniel Schneider of Natick R. D. and E. Laboratories who has asked us to review these matters is primarily interested only in the neat agent problem. This diffusion problem arises in assessing the definite amount of agent, $Q_b$, coming through a test membrane within a definite time period, $t_b$. Its relevance to monitoring and dosimetry is thus clear and needs no further comment.

The numerical solutions make clear both quanlitatively and quantitatively (for suitably chosen parameters) the overall expected behavior and the results are in overall agreement with observations. While for the polymer thickened agent droplet problem there is a more extensive region of scaling with regard to initial droplet radius, $R_o$, and membrane thickness, L, this is not the case for the neat droplet.[1] Specifically we showed[1-3] that simple scaling relations apply only for a rather limited parameter ranges: a) The more ubiquitous (under field conditions) case where the agent is deposited as an aerosol of tiny droplets which spread on the membrane, for which $R_o/L \ll 1$, the small droplet case. This case is essentially completely analyzed in references (1) and (4) and a quasi steady state analytical theory is given in reference (2) for the case that the agent solubility is sufficiently large. I am given to understand by Dr. Schneider that the scaling and applicability of this case is sufficiently well understood that no further comment is necessary here. (b) The more special case, we call the large droplet case, arises when $R_o/L \gg 1$. Note that the condition used for approximate

solution of this problem that the droplet is smaller than L cannot be correct for all time.[1] The radius of the sessile droplet decreases continuously with time and will ultimately become equat to or smaller than L (as the agent diffuses through the membrane) when the special scaling for the limiting ease must fail. In the next section we review the discussion of this special limiting case. It has been originally treated by us in reference (1) and (3). We shall treat it here more extensively in the next section showing that it arises from a singular perturbation of the original boundary value problem. In the last section we deal with the extension of this problem when evaporation from the sessile droplet surface is not negligible.

2. The large droplet case – negligible surface evaporation from the droplet.

We consider the moving boundary diffusion problem initially described in references (1) – (4). We use a slightly modified notation. All physical entities with dimensions, other than certain scaling variables such as $R_o$, L, etc. will be written with a carat over the letter denoting the entity. We will subsequently introduce suitably scaled, dimensionless variables denoted by letters without carats.

The concentration $\hat{c}$ of agent in the membrane at location $\hat{r}$, $\hat{z}$ at time $\hat{t}$ satisfies the diffusion boundary value problem[1-4]:

$$(\partial\hat{c}/\partial\hat{t}) = D \{(\partial^2\hat{c}/\partial\hat{r}^2) + 1/\hat{r} \, (\partial\hat{c}/\partial\hat{r}) + (\partial^2\hat{c}/\partial\hat{z}^2)\} \qquad (1)$$

in $0 < \hat{z} < L$ , $\hat{r} > 0$, $\hat{t} > 0$

with initial and boundary conditions

$$\hat{c}(\hat{r}, \hat{z}, \hat{t} = 0) = 0, \qquad\qquad\qquad (2)$$

$$c(\hat{r}, 0, \hat{t}) = c_o, \quad \hat{r} \le \hat{R}(\hat{t}) \qquad\qquad (3)$$

with $c_o$ the solubility of agent, i.e. the equilibrium concentration of agent in a membrane immersed in neat liquid agent at ambient fixed temperature and pressure and $\hat{R}(\hat{t})$ the time dependent sessile droplet radius. The sessile droplet is a spherical

cap with fixed contact angle $\Theta$ and volume $1/3\ f(\Theta)\hat{R}^3(t)$,

$f(\Theta) = \pi\sin\Theta(2+\cos\Theta)/(1+\cos\Theta)^{-2}$. Furthermore,

$$(\partial\hat{c}/\partial\hat{z})_{\hat{z}=0} = 0\ ,\ \hat{r} > \hat{R}(\hat{t}) \tag{4}$$

and

$$\hat{c}(\hat{r},\ L,\ \hat{t}) = 0. \tag{5}$$

The moving boundary of the spherical cap $\hat{r} = \hat{R}(\hat{t})$ is determined by the mass balance

$$\rho f(\Theta)\hat{R}^2\ (d\hat{R}/dt) = 2\pi D\int_0^{\hat{R}(\hat{t})} d\hat{r}\ \hat{r}\ (\partial\hat{c}/d\hat{z})_{\hat{z}=0}\ ;\ \hat{R}(\hat{t}=0) = R_0\ , \tag{6}$$

with $\rho$ the density of neat agent. We now introduce dimensionless variables:

$r = \hat{r}/R_0\ ,\ z = \hat{z}/L,$

$t = D\hat{t}/L^2\ ,\ R(t) = \hat{R}(\hat{t})/R_0\ ,$

$c(r,z,t) = \hat{c}(\hat{r},\hat{z},\hat{t})/c_0,$

$$\beta = 2\pi c_0/\rho f(\Theta)\ , \tag{7}$$

and a dimensionless parameter of smallness,

$\epsilon = L/R_0 \ll 1,$

into this boundary value problem.

One finds

$$(\partial c/\partial t) = (\partial^2 c/\partial z^2) + \epsilon^2\ [(\partial^2 c/\partial r^2) + 1/r\ \partial c/\partial r)] \tag{8}$$

in $0 < z < 1$, $r > 0$, $t > 0$;

$$c(r, z, 0) = 0\ , \tag{9}$$

$$c(r,0,t) = 1 \text{ for } r \le R(t), \tag{10}$$

$$(\partial c/\partial z)_{z=0} = 0 \text{ for } r > R(t)\ ; \tag{11}$$

$$c(r,1,t) = 0 \tag{12}$$

and

$$R^2 \, (dR/dt) = \epsilon \, \beta \int_0^{R(t)} dr \, r \, (\partial c/\partial z)_{z=0} \; , \qquad (13)$$

$$R(0) = 1.$$

The natural way to seek an approximate solution of (8) - (13) is to consider the singular perturbation in which the zeroth order solution for the concentration $c_o = c_o(z,t)$ satisfies (8) with neglect of the term in the square bracket on the r.h.s. of (8), i.e.

$$c = c_o(z,t) + 0(\epsilon) \qquad (14)$$

$$R(t) = R_o(t) + \epsilon R_1(t) + 0(\epsilon)$$

where

$$\partial c_o/\partial t = \partial^2 c_o/\partial z^2 \quad , \quad 0 < z < 1 \quad , \quad t > 0;$$

$$c_o(z,0) = 0 \quad , \qquad (15)$$

$$c_o(0,t) = 1 \quad ,$$

$$c_o(1,t) = 0;$$

and using (14) in (13)

$$dR_o/dt = 0 \quad , \quad R_o = 1 \quad , \qquad (16)$$

$$(dR_1/dt) = \beta \int_0^{R_o=1} dr \, r \, (\partial c_o/\partial z)_o = \beta/2 \, (\partial c_o/dz)_o \quad , \qquad (17)$$

$$R_1(0) = 0$$

The zeroth order solution of the boundary value problem (cf. (14) and (15)) has been given by us in reference (1) and also in reference (3) where it is given by the special case described by Eq. [7] on p. 284 which in our notation reads:

$$c_o(z,t) = \sum_{n=1}^{\infty} \{ \text{erfc} \, (2n + z/2\sqrt{t}) - \text{erfc} \, [(2(n+1)-z/2\sqrt{t})] \} \qquad (18)$$

$$R(t) = 1 + (\epsilon\beta/2) \int_0^t dt' \, [(\partial c_o(z,t')/dz)]_{z=0} \quad , \qquad (19)$$

The integrals given above are tabulated in standard tables.

To obtain a perturbation solution which holds for longer times one must introduce "stretched" coordinates, and find the "inner" and "outer" solution of this singular perturbation. We shall not carry out this rather dull but lengthy standard problem in applied mathematics.

Instead we point out that the zeroth order solution provides a limiting case, valid for very short times, when we further can replace the infinite series in (18) by its leading term for which

$$(\partial c_0/\partial z)_{z=0} \approx -[(\pi t)^{-1/2} (1 + 2e^{-1/t})] \quad . \tag{20}$$

Substituting this into (17) yields

$$R_1(t) = -\beta[(t/\pi)^{1/2} + \{2(t/\pi)^{1/2}e^{-1/t} - 2 \operatorname{erfc}(1/\sqrt{t})\}] \tag{21}$$

or

$$R(t) \sim 1 - \epsilon\beta[(t/\pi)^{1/2} + \{2(t/\pi)^{1/2}e^{-1/t} - 2 \operatorname{erfc}(1/\sqrt{t})\}].$$

In zeroth approximation the flux through the membrane at $z = 1$, (which in this approximation is exactly the same as the area averaged flux over the membrane) can be obtained from (18). We shall again only retain the leading order term in the summation (18) to calculate the zeroth order flux, which we write in dimensional form,

$$\hat{F}(\hat{t}) = -D (\partial\hat{c}_0/\partial\hat{z})_{\hat{z}=L}$$
$$\approx 2c_0(D/\pi t)^{1/2} c^{-\hat{L}^2/4D\hat{t}} \tag{22}$$

The absence of $R_0$ in (22) clearly shows that (22) can only apply for short enough times even if $\epsilon < < 1$. The use of (22) to calculate the reduced, dimensionless break through time, $\hat{t}_b D/L^2$, requires that

$$\hat{t}_b D/L^2 < \tau_L \tag{23a}$$

where $\tau_L$ is the time needed for the droplet radius to decrease by L, i.e. $R(\tau_L) = 1-\epsilon$. In zeroth order approximation the time $\tau_L$ is defined by the solution of the transcendental equation

$$\beta \left[ (\tau_L/\pi)^{1/2} + \{2(\tau_L/\pi)^{1/2} e^{-1/\tau} - 2 \, erfc(1/\sqrt{\tau_L})\} \right]$$

$$= 1. \tag{23b}$$

The special scaling in (22) also noted by Angelopoulos, Schneider and Meldon subsequently to us, in an unpublished report applies only well for sufficiently short times, even for $R_0/L > 1$.

3. The zeroth order solution of the large droplet case for non-negligible evaporation.

As shown in reference (4) if evaporation is not negligible (4) has to be replaced by

$$(\partial\hat{c}/\partial\hat{z})_{\hat{z}=0} + \hat{h} \, [\hat{c}(\hat{r},0,\hat{t})-\hat{U}] = 0 \, , \, \hat{r} > \hat{R}(t) \tag{24}$$

and (b) by

$$\rho f(\Theta)\hat{R}^2 \, (d\hat{R}/d\hat{t}) = 2\pi D \int_0^{\hat{R}(\hat{t})} d\hat{r} \, \hat{r}(\partial\hat{c}/\partial\hat{z})_{\hat{z}=0} \tag{25}$$

$$-\hat{R}^2 f(\Theta)\hat{\gamma}\rho$$

with $\hat{h}$ the evaporation coefficient characterizing the flat polymer-vapor interface, $\hat{U}$ the equilibrium concentration of agent in the vapor above the polymer, $\hat{\gamma}$ the (per unit surface area) evaporation coefficient of agent from a neat agent surface at ambient conditions. In the zeroth order approximation we neglect all diffusion for $\hat{r} > \hat{R}(\hat{t})$ so that the solution $c_0(z,t)$ is unaffected by (24) and is still given by (18). Denoting by $\gamma$ the appropriately scaled, dimensionless $\hat{\gamma}$ defined by

$$\gamma = L\hat{\gamma}/D \tag{26}$$

we can write the dimensionless equation (25) as

$$R^2 \ (dR/dt) = \epsilon \{ \beta \int_0^R dr \ r \ (\partial c/\partial z)_{z=0} - \gamma R^2 \} \qquad (27)$$

From (27) and (14), $R_0(t) = 1$, but

$$(dR_1/dt) = \beta \int_0^1 dr \ r \ (\partial c_0/\partial z)_{z=0} - 2\gamma R_1 \qquad (28)$$

with $R_1(0) = 0$. The solution of (28) is

$$R_1(t) = \beta \int_0^t dt' \ e^{-2\gamma(t-t')} \ (\partial c_0(r,z,t')/\partial z)_{z=0} \qquad (29)$$

which can be evaluated easily for short times using (20), the resulting integrals are all tabulated .

References

(1) Technical Reports from SUNYA sponsored by the U.S. Army Materials and Mechanics Research Center in Watertown, written by H.L. Frisch, 1984-1986.

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(6) G.O. Williams and H.L. Frisch, J. Stat. Phys. $\underline{63}$, 1035 (1991).